



Defense Threat Reduction Agency  
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# TECHNICAL REPORT

## Time-Dependent Temperature Measurements in Post-Detonation Combustion: Current State-of-the-Art Methods and Emerging Technologies

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## UNIT CONVERSION TABLE

U.S. customary units to and from international units of measurement<sup>\*</sup>

| U.S. Customary Units                             | <div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;"> </div> Multiply by </div> <div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;"> </div> Divide by<sup>†</sup> </div> | International Units                                     |
|--|---|---|
| <b>Length/Area/Volume</b>                        |   |   |
| inch (in)  | 2.54 × 10 <sup>-2</sup>   | meter (m)   |
| foot (ft)  | 3.048 × 10 <sup>-1</sup>  | meter (m)   |
| yard (yd)  | 9.144 × 10 <sup>-1</sup>  | meter (m)   |
| mile (mi, international)                         | 1.609 344 × 10 <sup>3</sup>   | meter (m)   |
| mile (nmi, nautical, U.S.)                       | 1.852 × 10 <sup>3</sup>   | meter (m)   |
| barn (b)   | 1 × 10 <sup>-28</sup>   | square meter (m <sup>2</sup> )                          |
| gallon (gal, U.S. liquid)                        | 3.785 412 × 10 <sup>-3</sup>  | cubic meter (m <sup>3</sup> )                           |
| cubic foot (ft <sup>3</sup> )                    | 2.831 685 × 10 <sup>-2</sup>  | cubic meter (m <sup>3</sup> )                           |
| <b>Mass/Density</b>                              |   |   |
| pound (lb)                                       | 4.535 924 × 10 <sup>-1</sup>  | kilogram (kg)   |
| unified atomic mass unit (amu)                   | 1.660 539 × 10 <sup>-27</sup>   | kilogram (kg)   |
| pound-mass per cubic foot (lb ft <sup>-3</sup> ) | 1.601 846 × 10 <sup>1</sup>   | kilogram per cubic meter (kg m <sup>-3</sup> )          |
| pound-force (lbf avoirdupois)                    | 4.448 222   | newton (N)  |
| <b>Energy/Work/Power</b>                         |   |   |
| electron volt (eV)                               | 1.602 177 × 10 <sup>-19</sup>   | joule (J)   |
| erg  | 1 × 10 <sup>-7</sup>  | joule (J)   |
| kiloton (kt) (TNT equivalent)                    | 4.184 × 10 <sup>12</sup>  | joule (J)   |
| British thermal unit (Btu)<br>(thermochemical)   | 1.054 350 × 10 <sup>3</sup>   | joule (J)   |
| foot-pound-force (ft lbf)                        | 1.355 818   | joule (J)   |
| calorie (cal) (thermochemical)                   | 4.184   | joule (J)   |
| <b>Pressure</b>                                  |   |   |
| atmosphere (atm)                                 | 1.013 250 × 10 <sup>5</sup>   | pascal (Pa)   |
| pound force per square inch (psi)                | 6.984 757 × 10 <sup>3</sup>   | pascal (Pa)   |
| <b>Temperature</b>                               |   |   |
| degree Fahrenheit (°F)                           | [T(°F) - 32]/1.8  | degree Celsius (°C)                                     |
| degree Fahrenheit (°F)                           | [T(°F) + 459.67]/1.8  | kelvin (K)  |
| <b>Radiation</b>                                 |   |   |
| curie (Ci) [activity of radionuclides]           | 3.7 × 10 <sup>10</sup>  | per second (s <sup>-1</sup> ) [becquerel (Bq)]          |
| roentgen (R) [air exposure]                      | 2.579 760 × 10 <sup>-4</sup>  | coulomb per kilogram (C kg <sup>-1</sup> )              |
| rad [absorbed dose]                              | 1 × 10 <sup>-2</sup>  | joule per kilogram (J kg <sup>-1</sup> ) [gray (Gy)]    |
| rem [equivalent and effective dose]              | 1 × 10 <sup>-2</sup>  | joule per kilogram (J kg <sup>-1</sup> ) [sievert (Sv)] |

<sup>\*</sup> Specific details regarding the implementation of SI units may be viewed at <http://www.bipm.org/en/si/>.

<sup>†</sup> Multiply the U.S. customary unit by the factor to get the international unit. Divide the international unit by the factor to get the U.S. customary unit.

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# **1. INTRODUCTION**

Measurement of energy release and the kinetics of energy release are of fundamental and ongoing importance. The energy release processes associated with explosives are of particular interest to the defense community, but measurements are often made difficult by the fast timescales involved. For gram-scale explosive samples, detonation is typically completed within several microseconds. Subsequent afterburning of under-oxidized detonation products can then produce a fireball that persists for several milliseconds. Unfortunately, the timescales associated with these processes limit the measurement techniques that can be employed. The high temperatures and pressures involved in the explosion also limit measurement options since any sensors employed must be able to withstand the extreme environment, or at least transmit the required data before being destroyed.

To characterize the energy release associated with explosions, it is desirable to determine both the temperature and pressure of the system. Over the many years that explosives have been studied, a variety of techniques have been developed to measure pressure in detonations and fireballs. On the other hand, temperature measurements have been less extensive, partly because sensors rugged enough to withstand the explosion have response times longer than the phenomena of interest.

Recent years have witnessed a number of efforts to develop methods capable of measuring temperatures in post-detonation combustion processes. The variety of approaches to this problem has been remarkable. Researchers have used pyrometry methods, atomic and molecular emission spectroscopy techniques covering the UV, visible, near-IR, and IR regions of the electromagnetic spectrum, laser-based absorption spectroscopy methods, and thermocouple measurements. Additionally, a number of efforts are underway to develop various types of sensor particles that can be entrained in the flow field of the fireball and undergo some chemical or physical change following exposure to elevated temperatures.

This report summarizes the presentations and discussions from the 2-day workshop on Time-Dependent Temperature Measurements in Post-Detonation Combustion, held October 2012; encouraged by the Defense Threat Reduction Agency's Basic Research Program, Thrust Area 4 on Science to Defeat WMD; chaired by Professor Nick Glumac of UIUC and Dr. William Lewis of UDRI. The report describes currently available methods for measuring temperatures during post-detonation combustion, compares the chief advantages and disadvantages of these methods, and identifies any emerging technologies. Each of the major approaches is detailed in Sections 2 – 6 below. We note that while atomic/molecular spectroscopy and laser spectroscopy are closely related, they are described in separate sections due to the unique challenges involved in utilizing laser probe beams in the vicinity of an explosion.

## **2. PYROMETRY**

### **2.1 GENERAL DESCRIPTION**

Pyrometry involves collection of radiation at well-defined, isolated spectral bands to infer temperature based on the spectral distribution of the light. While it is possible to use light collected in a

single spectral band to infer temperatures (i.e. single-color pyrometry), most techniques use multiple bands, with two bands being the most common. The irradiance measured by the detectors is then compared to the Planck radiation function. For single-color methods, an absolute (radiometric) irradiance measurement is required, but for multiple color methods, relative measurements are sufficient. In all methods, the irradiance in the target bands is assumed to be proportional to that of a blackbody, multiplied by some emissivity function which may be wavelength and temperature dependent.

## **2.2 EQUIPMENT AND SETUP**

There are many variants on the pyrometer for use in energetics systems. The most common is two detectors viewing the event through different interference filters. Light from the event can be split to the detectors using bifurcated or trifurcated fiber bundles – with some loss of light in the splitting process – or through dichroic mirrors which selectively reflect targeted spectral regions. Standard interference filters are currently available from the vacuum ultraviolet through the mid-infrared and can be centered on a wide range of wavelengths with bandpasses from <1 nm to 100s of nm.

The most common detectors that are used are photodiodes or photomultipliers. Photodiodes represent the most cost effective approach both in terms of the detector cost and the driver electronics. Some photodiodes offer excellent time response (ns-level). Silicon photodiodes cover the 200-1000 nm range with efficiencies peaking in the red region of the spectrum, while InGaAs photodiodes can be obtained for operation from roughly 1 to 1.7 microns, with extended ranges available on specialty variants. A common challenge with photodiodes is sensitivity, and in many cases there is not enough light to provide useful signal at the desired temporal resolution. Avalanche photodiodes (APDs) are seeing more common use in photometry and pyrometry, since these detectors have nearly three orders of magnitude higher sensitivity than PIN photodiodes, are available in silicon and InGaAs variants, and can have fast temporal response. Detector and driver electronics are significantly higher cost than PIN variants, but the detectors are robust and suitable for field use.

Photomultipliers (PMTs) remain in use as pyrometer detectors in some systems. PMTs, based on the photoelectric effect, represent a well-established and widely available technology with very high sensitivity. Both APDs and PMTs offer single photon sensitivities. PMTs offer large area detection while maintaining very fast temporal response, which can be sub-nanosecond. Challenges associated with PMTs, however, are many. PMTs must be shielded from stray magnetic fields, and the tubes are somewhat fragile (at least more so than photodiodes). Tubes require high voltage sources and careful attention to signal processing to avoid spurious signals. These challenges are generally readily addressed with careful practice. A more significant limitation is spectral range which is determined by the photoelectric properties of the photocathode which must eject electrons when photons above a certain energy threshold are incident on the surface. Efficient multialkali photocathodes are available for the VUV, UV, and blue spectral ranges. Efficiency tends to decay from green towards red light for most photocathodes. Sharp cutoffs at 650 and 850 nm are common. Near-IR PMTs with InP/InGaAs photocathodes have response out to at least 1.6 microns with an order of a magnitude loss in sensitivity and considerable increase in cost. The near-infrared, where measurements are often most desirable, is where PMTs are least efficient both in terms of performance and price.

Imaging detectors can also be used in pyrometry, providing spatial information as well as spectral. CCD and CMOS chips have similar spectral responses from 200 – 1000 nm. InGaAs arrays can



extend the technique to the near-infrared. Thermal imaging cameras based on InSb, HgCdTe, and similar materials in the mid-wave infrared (MWIR) from 3-5 microns, and microbolometer arrays in the long-wave infrared (LWIR) from 8-12 microns are widely commercially available. These cameras typically integrate light over a single wide spectral band and are calibrated radiometrically to yield a 2-D map of temperature. For both visible and infrared approaches, multiple bands can be monitored by either using multiple cameras or imaging multiple (usually two) identical images onto the same chip, but with different bandpass filters on each image. While camera speeds are increasing every year, at present, silicon-based detectors offer the potential for very high speed imaging, approaching 1 million frames per second for smaller arrays (e.g. 256 x 256) with 10-100 kHz on larger arrays being common. Infrared camera speeds are markedly slower, with 1-10 kHz representing the current leading edge of the technology. Visible and UV light systems with intensifiers (e.g. ICCDs or sets of ICCDs in a framing camera) can obtain single frames or short sequences of frames with time resolution approaching the nanosecond level. Analogous systems for the near-IR are not yet available.

Calibration of pyrometry techniques is primarily done using blackbody sources which are widely available. The most basic commercial blackbody sources use kanthal or nichrome resistive elements around a ceramic or graphite cavity. These systems are rugged, air-stable, and long-lived, but are typically limited to about 1200 °C. Calibration at higher temperatures can be performed using expensive high temperature blackbody sources which can operate at up to 3000 K or, more commonly, tungsten strip or wire lamps. In the latter case, special care must be taken to account for the emissivity variation of tungsten with wavelength. This function for tungsten decays monotonically from blue to infrared, and the function has some temperature dependence as well. In addition, care must be taken to insure that there is no spectral bias in the collection optics. A diffuser is often used in such setups.

### **2.3 ADVANTAGES**

Pyrometry is one of the simplest and least costly techniques to incorporate for temperature estimation. Signal processing is straightforward, at least in the most basic form of the measurement. Calibration can be performed regularly with inexpensive sources. The time response can be outstanding. Non-imaging techniques can achieve nanosecond level precision. Detectors are inexpensive and robust. Costs are low enough such that expendable devices are possible for some applications, and suitably armored devices can be embedded within the blast event. Imaging techniques can produce a 2-D spatial map of temperature, and when combined with high speed imaging, maps can be produced with interframe times as low as 1 microsecond. Measurements can be made at great distances from the event. A wide variety of detectors can be used.

### **2.4 CHALLENGES**

The simplicity of the pyrometry setup and signal processing creates a deceptive situation. While it is very easy to get a numerical value for “temperature” from a pyrometry measurement, the interpretation and accuracy of this measurement is far more complicated. The pyrometry signal can be compromised by several effects, and even when all these are taken into account, the meaning of the “temperature” derived from a measurement is often non-trivial.

#### **2.4.1 Spectral interferences**

Thermal emission from solids generally follows a mostly continuous spectral distribution related to the Planck function. Gas emission, on the other hand, most often exhibits emission that may have a

weak underlying continuum with strong emission in isolated atomic lines and/or molecular bands. For example, lines from sodium, potassium, and calcium are commonly seen in spectra from explosive events, even though these elements may only be present as impurities from processing. Calcium hydroxide (CaOH) is a common emitter seen in propellant and explosive spectra with bands in the green and red. In addition, metallized systems will show bands due to intermediates such as the well-known AlO and BO<sub>2</sub> bands in the aluminum and boron systems. These bands dominate the underlying continuum on which the pyrometry measurement relies. Thus, it is critical that the spectral bands be chosen to avoid molecular interferences. For many systems, such avoidance would require operation in the near-infrared, which may limit the use of photomultipliers in some cases. Several investigators stress that it is important to take emission spectra of the event, even at low resolution, even if the spectra are time-integrated, to verify that the regions of the spectrum used for pyrometry are free of spectral interferences. Regions around the sodium D doublet (589 nm) and the potassium near-infrared doublet (767-770 nm) should especially be avoided.

#### **2.4.2 Line of sight and field of view**

Detectors average irradiance over some field of view (FOV) determined by the detector size and collection optics. For imaging diagnostics, the spatial FOV is easy to quantify, but for non-imaging approaches, care must be taken to quantify the portion of the field that is sampled by the detector. Light from the entire FOV can reach the detector, though efficiency of detection varies with location in the FOV in accordance with the solid angle subtended by the detector. Points nearer the detector and closer to the optical axis are more efficiently collected than those farther and off-axis. Unless the entire FOV is spatially homogeneous, the signal read by the detector will consist of light from many rays which may represent a range of temperatures.

In a similar fashion, the light that reaches the detector along any particular ray in the FOV may consist of contributions from several distances along the ray. This effect, which is often called, “line-of-sight” averaging is especially complex in energetic systems where the opacity of the event can vary spatially and temporally (see Section 2.4.3 below).

The spatial averaging effect has a significant role in the interpretation of the single value of “temperature” that the detector (or pixel) yields. While all volume elements in the FOV can reach the detector, they are not equally represented in the signal. Four considerations are of primary importance. First, the Planck distribution has a  $T^4$  dependence in radiance. Accordingly, hotter ensembles of emitters emit more photons than cooler ensembles, and thus they will be disproportionately represented at the detector. This effect often leads investigators to interpret pyrometric measurements as indicative of the hottest regions in the FOV, or at least strongly biased towards these regions. Second, the radiance from a given location is proportional to number density of emitters. Since soot is a common emitter in energetic fireballs, and since soot concentration varies spatially and temporally, these variations can affect the irradiance registered by the detector. Third, when optical depth is important, light from ever distant regions of the FOV is attenuated, and if opacity is strong, then emission from many regions in the FOV will not reach the detector at all. Fourth, as mentioned above, efficiency of light collection from any spatial region will be proportional to the solid angle that the detector subtends.

### 2.4.3 Emissivity vs. wavelength and optical depth

Emission from any real event does not exactly follow the Planck distribution but is instead modified by the emissivity which is a function of both wavelength and temperature for any given emitter. When investigating emitting particle clouds that have significant optical transparency, the emissivity ( $\epsilon$ ) may vary strongly with wavelength, and some have proposed a  $\epsilon \sim 1/\lambda^2$  [1] dependence, while experiments have shown varying values from grey behavior to  $1/\lambda$  [2]. High temperature data on the function  $\epsilon(\lambda, T)$  for most emitters at elevated temperatures is incomplete. Thus, pyrometry of clouds at low optical depths is especially challenging due to complex spatial averaging and uncertainties in emissivity. It is important to note that as optical depth approaches the thick limit, thermal emission will approach greybody behavior, and so the grey assumption in optically thick clouds may be most appropriate, though it yields a “temperature” estimation that would be relevant only for the surface or near-surface of the cloud.

### 2.4.4 Detector dynamic range

Because of the  $T^4$  dependence on radiance from a thermal emitter, the dynamic range of the detector will limit the range of temperatures that is observable. Thus, for a two-color system, the choice of optical settings (exposure times, use of neutral density filters, lens f-number) and spectral bands used will generally be tailored for a certain temperature range which is relevant for typically a certain portion of the event. In some cases, it may be useful to include additional or redundant spectral channels of detection that are set up such that they are saturated at early times but can recover to provide useful signal at later times when temperatures are lower. In this fashion, the temperature range and duration of the measurement can be extended.

### 2.4.5 Gases vs. particles

At sufficient optical depth, a high temperature gas cloud will emit with the spectral distribution of a blackbody. Thus, in a dense mixture of gases and particles, there may be some question as to how well the measured pyrometric “temperature” corresponds to the gas-phase temperature. In general, condensed phases will emit much more strongly than gases under most relevant conditions, and thus the pyrometry temperature is often referred to as the temperature of the “condensed phases.” In cases where there is a temperature distribution in the field (e.g. burning aluminum particles), there may even be a difference in condensed phase temperatures due to spatial averaging effects. It is important to note that any use of the pyrometric temperature to infer local gas phase temperatures requires a number of assumptions that may or may not be relevant. Detailed modeling of the flow in the FOV is likely required to support such assumptions.

### 2.4.6 Calibration and electronics challenges

While the optical and electronic system appears simple, care must be taken to avoid bias in several areas. Detector linearity is important, and the linearity needs to be verified over the entire range of signals that is encountered. Photomultiplier and photodiodes show a saturation response curve where signal continues to increase with irradiance, but varies from linearity. Care should be taken to avoid these regions. In addition, spectral bias may be present at different spatial locations in the flow due to collection optics. Careful measurement using sources at different spatial locations can assess this potential problem. Finally, it is important to note that while a single temperature measurement from a source provides a calibration constant for a two color pyrometer, it is important to vary source

temperature to ensure that this “constant” does not vary with temperature, which would indicate spectral bias or detector non-linearity issues.

## **2.5 EMERGING TECHNOLOGIES**

### **2.5.1 Color cameras.**

Color camera chips contain filters that isolate three spectral regions loosely associated with the red, green, and blue spectral regions. Densmore and co-workers [3] have used a commercial high speed imaging camera for pyrometric measurements of explosive fireballs. Their work addresses many of the important signal processing issues associated with extracting photometric data from the image files produced by the cameras. As such, the work makes three-color pyrometry accessible for almost any color system.

An important note which may limit the applicability of the technique in some applications is that the bands used in color cameras are in the visible region where molecular interferences may be present in some systems. In situations where such interferences are prominent, the technique may have limited utility.

### **2.5.2 Embedded probes.**

Spatial averaging and optical depth are perhaps the largest barriers to accurate characterization of a fireball with pyrometry. External probes of optically thick clouds will characterize only surface or near-surface conditions. As clouds thin, spatial averaging becomes a factor and the single measurement becomes a convolution over signals from many points. Probes embedded within the fireball can address some of these issues, and this approach has been used by Pahl [4], Albro [5], Lynch [6] and others. Armored optical probes are distributed within the fireball region, and the signal is extracted with fiber optic cables such that no electronics are exposed. Each fiber can lead to a two-color pyrometer, or fiber arrays can be imaged onto one or two cameras through bandpass filters. Lynch [6] used an approach where each fiber was aligned on the inlet slit of an imaging spectrograph read out by a framing camera. An approach developed by Pahl [4] involves using a stop in the FOV of each probe, thus isolating the spatial region over which the emission is collected. In this fashion, spatial averaging and optical depth effects are reduced, and the signal from each probe is representative of the emission from an isolated volume within the event. Collection of multiple probe signals would then allow true three dimensional spatial resolution with temporal resolution as well. Of course, the cost of such a system will be larger than a single probe system.

### **2.5.3 Simultaneous optical depth characterization**

Albro and co-workers at NAVAIR [5] have developed a tool to simultaneously measure local optical depth and pyrometry signals from nearby regions. In this way, the optical depth effects can be more readily quantified in the signal processing, leading to more insight into spatial distribution of emitters that yields the pyrometry signal.

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### **3. ATOMIC & MOLECULAR SPECTROSCOPY**

#### ***3.1 INTRODUCTION AND GENERAL ADVANTAGES AND CHALLENGES OF SPECTROSCOPY***

Atomic and molecular spectroscopy methods are an attractive approach for measuring temperatures in post-detonation combustion for several reasons. Such techniques are capable of recording the dynamics of very fast processes with modern instrumentation; ns or even faster time resolution is now routine with many detectors. Additionally, spectroscopy methods have been used for many years to study flames [1] and plasmas [2], yielding a large body of work with which to compare. Spectroscopic measurements can utilize either absorption or emission, and can be conducted in the ultraviolet (UV), visible, near-infrared, or infrared (IR) regions of electromagnetic spectrum. Since the advantages and difficulties associated with the measurements depend upon what region of the electromagnetic spectrum one chooses to work with, we will consider IR and UV/visible/near-IR investigations separately.

With respect to the study of post-detonation combustion, emission spectroscopy has been employed far more extensively than absorption. This is largely due to the fact that the fireball itself is a very intense, and readily available, light source. Not only is the emitted light convenient for emission experiments, but finding a light source significantly brighter than the fireball in order to then obtain absorption spectra is quite difficult. To the authors' knowledge the only successful attempts to do so have utilized laser light, and are thus discussed in Section 4.

One very important advantage of any emission spectroscopy-based method is that an emission spectrum can be collected at a great distance from the explosion, which carries obvious safety advantages for both research personnel and instrumentation. Additionally, the instrumentation required for emission experiments is generally easy to use, requiring only line-of-sight to the explosion. And fiber optics can even be used to route light from collection optics (such as lenses and telescopes) to instrument inputs to make matters even more convenient. A significant disadvantage of all emission spectroscopy techniques is that some minimum temperature is generally required in order to efficiently populate excited states and generate emission spectra. An additional concern is that emission spectra are generally spatially averaged

over the luminescent region sampled by the collection optics. When the emission spectra from colder regions are added to those from hotter regions, the result is an “apparent temperature” that can be several hundred Kelvin different from the average temperature [3]. This phenomenon imposes a fundamental limit on the absolute accuracy of temperature measurements made on non-isothermal flames such as those typically found in turbulent post-detonation fireballs.

Finally, it has been shown that post-detonation fireballs are remarkably optically dense [4-9], with typical attenuation pathlengths of mm – cm [9]. Consequently, it is important to keep in mind that emission spectra collected from outside a fireball correspond to the material near its surface. Although normally thought of as a disadvantage, recently some of the authors have tried to exploit the optical density of the fireball in order to obtain space-localized measurements using fiber optics to collect light from points inside the interior [10].

### **3.2 ADVANTAGES AND CHALLENGES OF SPECIFIC SPECTROSCOPY TECHNIQUES**

#### **3.2.1 Molecular emission spectroscopy in the IR**

Some of the first emission spectroscopy work to be done on post-detonation combustion involved recording the IR emission spectra [11-13]. It was noted [12,13] that while much of the emission in the IR was well-described by a Planck distribution, molecular emission bands (such as those from CO<sub>2</sub>) could also be detected. Work in the IR region, which corresponds to rovibrational molecular transitions, carries the advantage that many detonation and combustion products (such as CO, CO<sub>2</sub> and H<sub>2</sub>O) have very intense IR transitions. Interpretation of the data is typically straightforward because bands for small molecules such as CO<sub>2</sub> and H<sub>2</sub>O have been the subject of extensive study for many years, and their transition frequencies/wavelengths and intensities are typically well known. Provided that the observed vibrational bands are rotationally resolved, or at least that the contours of the P, Q, and R branches of the bands can be seen, a rotational temperature can in principle be extracted independently from each band present in the spectrum. Vibrational temperatures can also be obtained if emission bands are present from more than one upper energy state *e.g.* if both  $v=0 \leftarrow 1$  and  $v=1 \leftarrow 2$  bands of CO<sub>2</sub> are observed

This approach has a number of advantages: it relies upon species which are almost always present following detonation, uses transitions which are very intense, and has built-in measurement redundancy because temperatures are obtainable from multiple species and bands. The main disadvantage of the approach is that air is not transparent in the IR. Many of the same species mentioned above (CO, CO<sub>2</sub> and H<sub>2</sub>O) are present in small concentrations in air and absorb the light emitted by the fireball on its way to the detector. Over practical safe stand-off distances (10-1000 m), the absorptions can be quite significant. Hence, in order to analyze the IR emission spectrum quantitatively, calculation of the absorption contribution from the air over the stand-off distance is required [12, 13]. In order to do this, the stand-off distance and atmospheric conditions (humidity, CO<sub>2</sub> concentration, etc) must be determined quantitatively. Additional disadvantages include the very limited measurement rates and significant expense of currently available spectrometers. Most of the work in this area has been performed with FTIR spectrometers which have measurement rates typically 50 Hz or less and cost >\$100k. Faster data acquisition should be possible with dispersive instruments, although these often come at the cost of reduced resolution and spectral range. Regardless of the type of instrument employed, another possible disadvantage of this method is the detailed spectroscopy knowledge required to analyze the IR spectrum. Finally, like all emission techniques elevated temperatures are required in order to generate emission

signals. The minimum temperature required depends upon the sensitivity of the detector of course, but a minimum temperature of 1000 K would be typical [13] for use of molecular emission in the IR.

### **3.2.2 Molecular emission spectroscopy in the UV/visible/near-IR**

Many subsequent investigations using emission spectroscopy have utilized spectral features in the UV/visible/near-IR to interrogate the temporal dynamics [14-20]. This region of the spectrum corresponds to electronic transitions of both atomic and molecular species, although we note that vibrational overtones and combination bands can be observed in the near-IR. A significant advantage of working in this region of the electromagnetic spectrum is that air is transparent over enormous distances (km) between approximately 200 – 800 nm, so the exact stand-off distance and atmospheric conditions do not need to be taken into account. At wavelengths outside this range, molecular oxygen begins to absorb and at the longer wavelengths, vibrational overtones of H<sub>2</sub>O begin to appear also. Additional advantages are that spectroscopy equipment for these wavelengths is readily available, easy to use, and modern equipment has very high performance to cost ratio. Spectrometers with measurement rates of 1 kHz are commercially available for <\$3k, and systems with data collection rates in excess of 50 kHz can be built for <\$20k. More expensive detectors can reach 1 MHz or even faster rates.

An important characteristic of electronic emission spectroscopy in combustion environments is that the chemical species observed in the emission spectrum are somewhat more exotic than those typically found in the IR spectrum. A strong electronic emission intensity requires an excited state with energy low enough to be populated at flame temperatures, good Franck-Condon overlap between the emitting species in the upper and lower states, and the absence of any processes (such as internal conversion) that can efficiently compete with photon emission. Consequently, the species most often observed are various diatomics, radicals, and atoms. In combustion environments, OH, CH, and C<sub>2</sub> emission bands are quite common [1]. Emission lines from Na atoms are ubiquitous, but Li, K, and Ca are also often observed if the sample has even a small impurity containing these elements. For metalized explosives, emission lines from metal atoms and metal monoxides (AlO, BaO, etc) are often found. Large broadband emissions from particulates are also common. One consequence of all this is that the spectrum, while information-rich, can often be quite complex with multiple overlapping bands, large broadband emissions, and strong signals from trace impurities [14,16-20].

Nevertheless, in principle any molecular band observed in the spectrum can be used to obtain a temperature. In each band, multiple lines are observed corresponding to different pairings of vibrational states in the upper and lower electronic manifolds. The relative intensities of the various lines in the vibronic band (or just its contours if the lines are not fully resolved) can be used to determine a vibrational temperature for the molecule. This process can be repeated for each molecular band in the spectrum in order to obtain redundant temperature measurements, provided that the emitting species for the band is known, the band is not too obscured by some other signal, and that the Franck-Condon overlap integrals for the various pairings of vibrational states are available or can be calculated. Additionally, the experimenter must be careful to either avoid self-absorption effects, or account for them in the analysis of the vibronic band. Unfortunately, sorting all this out often requires a very thorough knowledge of spectroscopy, and if Franck-Condon overlap integrals must be calculated also, then knowledge of computational chemistry is needed as well. The fact that data analysis can be so daunting is a significant disadvantage.

Another very significant challenge associated with this method is that the various degrees of freedom of a molecule observed in emission may not be in equilibrium; for example, the vibrational temperature of a molecule may differ from its translational or rotational temperature. Such a situation can arise when highly exothermic reactions produce emitting species in excited states *i.e.* chemiluminescent reaction products. If the reaction products emit before they equilibrate with the surrounding material, its emission band yields an apparent temperature related to the associated chemical process that originated it rather than the surrounding temperature. Examples of this behavior have been observed in flames [1] and it is likely to occur in fireballs as well. Alternatively, mismatches between vibrational and translational or rotational temperatures can occur if the system evolves too rapidly for equilibrium between the molecular degrees of freedom to be fully established, *e.g.* plasmas. To some extent these difficulties are avoided when redundant temperatures are obtained from multiple species and bands, but clearly care must be exercised.

One very useful adaptation of the molecular emission technique that avoids the need for the intensive data analysis needed to extract temperatures (and also many thermal vs. chemiluminescence concerns) is to use the spectra to track chemical dynamics instead. While not a temperature measurement technique *per se*, this approach bears mentioning here because it is often used in conjunction with temperatures obtained simultaneously via pyrometry or by atomic emission spectroscopy (see Section 1 and Section 3.2.3). In this approach, the emission spectrum is analyzed qualitatively but chemical dynamics are tracked quantitatively; that is the various peaks and bands in the spectrum are identified and their intensities are plotted as a function of time in order to obtain kinetics information about chemical processes occurring in the fireball [14,15]. This approach has been used in a number of investigations to examine chemical dynamics in fireballs produced following detonation of explosive charges containing aluminum [14-16,18-20] or silver [16] by tracking the time dependence of atomic Al lines, AlO bands, and atomic Ag lines.

Regardless of what vibronic bands are observed, or how they are used, molecular emission spectroscopy's main advantages are high data collection rates, the low cost, ease of use, and wide availability of the instrumentation, and the convenience of not needing to account for absorption effects in air. The chief disadvantages of the method are the difficulty of the data analysis if temperatures are to be extracted, the care that must be taken to avoid confusing thermal and chemiluminescent emissions, and the fact that like all electronic emission spectroscopies, elevated temperatures are required. Temperatures in the vicinity of ~2000 K are generally required to generate strong emission signals [15-18].

### **3.2.3 Atomic emission spectroscopy in the UV/visible/near-IR**

As mentioned above the spectra obtained in electronic emission spectroscopy of post-detonation combustion can often be quite complex, with many (frequently overlapping) bands. This complexity, combined with the presence of strong signals from impurities and broadband emissions can make interpretation of the spectrum difficult, particularly when the goal is to extract temperatures from the vibronic bands observed. An alternative approach that has been developed is to utilize atomic emissions for the temperature measurements [16-20], with the molecular emission bands optionally employed to simultaneously track chemical dynamics as described in Section 3.2.2. This approach for measuring temperatures can be employed even in the most congested and difficult-to-assign spectra since the atomic emissions are simply superimposed on top of the other spectral features.



The determination of an apparent temperature from atomic emission lines is much simpler than that for molecular bands since atomic species do not have vibrational or rotational degrees of freedom. Thus the transitions are entirely electronic in nature. The temperature is measured using the relative intensities of two or more emission lines from the same atom [15-20]. Provided that two lines originate from different upper energy levels, the ratio of their intensity is related to the electronic temperature by a single simple equation. Consequently, this approach does not require extensive knowledge of spectroscopy, and the data analysis is little more complex than that used in pyrometry. However, as this approach relies upon the assumption that the electronic temperature of the atomic “thermometer” is equilibrated with the surrounding flame temperature, care must be taken to be certain the assumption holds (for the same reasons discussed in Section 3.3.2).

Atomic emission lines produced by species already present in the sample, such as Na impurities, can be used as long as at least two lines from different energy levels are present. Or if no suitable signals already exist in the spectrum, they can be introduced by doping the explosive charge with a small amount of an inorganic salt containing the element of interest. The concentration of the dopant must be kept low to avoid perturbation of the system under study as well as any self-absorption effects. Doping with barium nitrate has been used to measure the post-detonation combustion temperatures of a number of explosive formulations to date [17-20]. Certainly, elements other than Ba can be used as “atomic thermometers” although some are more useful than others. The key requirements are these: the atom should have several known emission lines (at least two) within the spectral range of the spectrometer employed, the lines must originate from different upper energy levels, and the energy levels must be low enough in energy ( $< 3$  eV) that they can be populated at typical flame temperatures. It is also desirable that the energy levels be 0.5 - 1.5 eV apart (so that the intensity ratio is sensitive to the flame temperature), and that the Einstein A coefficients associated with the upper levels be  $\geq 10^7/\text{s}$  in order to produce strong emission signals [17].

This approach is interesting because it retains all of the advantages of molecular emission spectroscopy (fast data collection, widely available, easy to use, and relatively inexpensive instruments, and insensitivity to air), while addressing one of its chief disadvantages: the daunting data analysis. Moreover, the fact that the molecular bands used to monitor chemical dynamics are collected in the spectrometer simultaneously with the atomic lines used to determine temperatures results in a very powerful combination indeed. For example, with aluminized RDX charges this combination technique can record Al oxidation processes, combustion of soot and organics, and flame temperature simultaneously [18,20] with no additional effort on the part of the experimenter. It is not difficult to imagine how the combination of these pieces of information can be more useful than the sum of the parts so to speak.

These advantages do come at a cost however. An obvious disadvantage of this method is that “thermometer atom”-doped charges must be made unless a suitable impurity already exists in the formulation under study. Additionally, the fact that atoms in multiple electronic excited states must be produced necessitates a minimum temperature of  $\sim 2500$  K in order to make an accurate measurement [18,19]. As mentioned above, the assumption that the electronic temperature of the dopant is in equilibrium with the flame should also be checked to ensure accuracy.

### 3.3 EMERGING TECHNOLOGIES

The fundamentals of atomic and molecular spectroscopy have been established for many years now. Almost all progress in the field of spectroscopy now entails either the discovery of new chemical species and their properties, or the development of advanced detection methods. But the basic description of the optical and physical processes involved in spectroscopy seems quite mature.

With respect to spectroscopy techniques for the study of temperature in post-detonation combustion, it seems correspondingly unlikely that emerging technologies will be based upon entirely new optical or physical phenomenon. Rather, rapid progress is likely to be realized by applying existing spectroscopy concepts to the problem and exploiting the extensive body of knowledge that already exists from the field to the study of detonation and post-detonation chemistry. Given that spectroscopy has been immensely successful in studying combustion and flames, this would seem to be fertile ground indeed. The emerging technologies in this area are the low-cost, high performance spectrometers (typically based upon CCD detector arrays) that are now becoming inexpensive (measurement rates of 1 kHz for <\$3k; 50 kHz for \$20k). In time, the performance available at such modest cost is only expected to increase, opening up entirely new possibilities for studying fast combustion phenomenon with spectroscopic methods. The increasing convenience of these measurements, combined with the ingenuity of the experimenters in adapting them to post-detonation studies, will likely make a substantial impact in the coming years.

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## 4. LASER-BASED METHODOLOGIES

### 4.1 INTRODUCTION

Laser-based methods are widely used in combustion research to generate point and 2-D field measurements of temperature. The most widely used techniques are laser-induced fluorescence (LIF), Raman scattering, Rayleigh scattering, and Coherent-Anti-Stokes-Raman Scattering (CARS) [1,2]. LIF, Raman, and CARS all probe a target species at a location in the flame and generate a spectrum from which the rotational or vibrational population distribution of the target species can be obtained, yielding the temperature. Rayleigh scattering of a laser beam or sheet is proportional to number density, and, if pressure is known, then temperature can be extracted if one can estimate the relative local composition of scatterers. CARS is generally a point measurement, and Raman is most often a point or line due to low signal levels. LIF and Rayleigh scattering have seen wide use as 2-D temperature probes.

Lasers produce short, high-energy pulses that provide spectral irradiances that can be orders of magnitude higher than incoherent sources. Pulsed lasers with pulsewidths of a few nanoseconds are common. Picosecond and femtosecond lasers are commercially available. Repetition rates range from the most common 10 Hz to over 1 MHz for some commercial picosecond and femtosecond lasers.

## **4.2 ADVANTAGES**

Laser methods have shown the ability to probe ground states of major and minor species, generating well-resolved distributions of population within rovibronic bands. Temperatures generated with these tools can be highly accurate, especially in the case of CARS measurements where 1-2% accuracy has been achieved. LIF, Raman, Rayleigh, and CARS all are point measurements since detection and excitation rays intersect at a single point. In this way, line of sight effects are eliminated. Temporal precision of laser measurements is extremely good.

## **4.3 CHALLENGES**

Two primary issues complicate use of laser-based tools in energetics systems: short transient events, and optically dense media. In many applications, laser-based temperature measurements average over many shots taken at low repetition rates of, for example, 10 Hz. Since energetics events often last a few milliseconds or less, one might expect a single laser pulse per event, which provides excellent temporal precision (e.g. ns pulsewidth), but little temporal range. In optically thick media, the challenge of getting the laser pulse to the target area and extracting the signal pulse out is daunting, and conventional optical approaches are unlikely to work.

Laser systems are generally quite costly and delicate. While laser diagnostics have been applied to challenging industrial and aerospace environments (e.g. internal combustion engines, coal combustors, rocket nozzles, combustion chambers, etc.), there has been substantially less effort in applying laser temperature measurements to short, transient explosive events.

Despite these challenges a few laser-based temperature measurements have been performed in explosive test environments, and work has been done on tools that may enable further advances in this field.

## **4.4 EMERGING TECHNOLOGIES**

### **4.4.1 Femtosecond lasers and techniques**

Femtosecond lasers offer spectrally broad bandwidths in high energy pulses that can be used in a variety of optical diagnostics. Researchers including Kearney et al. at [3] Sandia have applied CARS in a hybrid femtosecond/picosecond approach that yields single shot rotational temperatures at 1 kHz repetition rates with very high accuracy. The group has also done considerable work in developing probe designs to perform CARS measurements in pool flames where constraints are similar to those involved in in-fireball measurements. CARS techniques are sensitive to media in which there is a great deal of scattering or attenuation, but by use of localized probes and short path lengths, these issues can be mitigated.

These techniques remain somewhat costly, and this fact limits the ability to perform multiple measurements in the same field. However, they do appear exceptionally suitable for single point, time-resolved measurements in a combustion field with very high accuracy.

### **4.4.2 Modeless dye laser absorption**

Laser sources offer exceptional spectral brightness, and there is the potential to pass a measurable amount of light through even fairly optically thick media. Some researchers have applied this technique to generate line-of-sight averaged spectra through optically dense clouds of explosion products, yielding

atomic and molecular spectra from which path-averaged temperatures can be derived [4]. These measurements used nanosecond lasers with a modeless dye laser to generate broadband spectra that were directed into a spectrometer using fiber optics. Transmitted beams from multiple spatial locations as well as a reference beam could be obtained in a single exposure with good time resolution, but only a single shot per test. Similar techniques could be possible with broadband femtosecond lasers. Though the tests were performed in the visible spectral region targeting Al, Ti, Ca, and AlO, extension to the ultraviolet and infrared by broadband frequency doubling [5] and shifting techniques appears possible.

#### **4.4.3 Pulse burst lasers**

While picosecond and femtosecond lasers offer potentially very high repetition rates, the pulse power is typically low and the cost remains very high. A modification of the standard flashlamp-pumped crystal laser where the cavity Q-switch is rapidly modulated can produce a series (burst) of high energy (10s of mJ) pulses spaced microseconds apart within the flashlamp pulse which lasts several hundred microseconds [6]. If each pulse generates a single measurement, then such a tool would enable measurements approaching the megahertz range but with high enough laser power to drive dye lasers or non-linear crystal devices, or to generate sheets of light from which 2-D scattering or absorption data can be extracted.

#### **4.4.4 Fiber probes**

For techniques sensitive to opacity, local measurements are likely the only possible means for obtaining temperature data, and these would require probes that are at least moderately non-intrusive and yet can bring the laser beam in and signal back out without inducing excessive noise. The setups must also be robust enough to withstand the conditions in an explosive test. Koch et al. [7] demonstrated one such approach using a differential optical amplifier as an infrared source and looking at time resolved water vapor detection. To minimize broadband fiber noise, the investigators used single mode fibers, which required careful alignment but produced very high signal to noise ratio spectra with excellent time resolution. The probe structure was not entirely non-intrusive for the small scale charges studied, though the path of explosive gases to the measurement volume was essentially unobstructed. In larger scale tests, this robust probe design would be even less intrusive. In addition, future research may lead to refined approaches with smaller footprint and projected area. Similar techniques should be applicable to other laser diagnostic approaches.

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## **5. PHYSICAL PROBES**

### **5.1 OVERVIEW AND ADVANTAGES**

Physical temperature probes such as thermocouples and cold wire probes are widely used to measure temperatures in laboratory and industrial settings, and for good reasons. Thermocouples are so inexpensive as to be disposable, provide a precise measurement location, can measure temperatures anywhere from sub-ambient to >1500 K, and are easy to use. Data analysis is as simple as using a table provided by the manufacturer that relates the thermocouple output voltage to the temperature. Cold wire probes are a similar technology except that the resistance of the wire as a function of temperature rather than an output voltage is used to make a measurement.

### **5.2 CHALLENGES**

The powerful advantages of physical probe techniques are counterbalanced by some disadvantages. The probes may be subject to radiative and catalytic heating effects, which are not negligible at fireball temperatures, and their presence can also perturb mass and heat flow [1]. The most serious issues are that the thermal response time of the probe can often be longer than the duration of the explosive event under study, and that the probe may be destroyed during the explosion. The latter is not too serious a problem given the low cost, provided the probe can survive long enough to transmit the required data before it is destroyed. For reference, during small scale explosive tests, thermocouples placed in the far field with diameters in the range of 25-50 microns are typically destroyed during explosions, but those with diameters of 125 microns or greater usually survive [2].

#### **5.2.1 Thermal response timescales**

The thermal response time and the durability of the probes are of course related. Thicker wires, armored sheaths, and support substrates can all improve the likelihood that the probe will survive the explosion, but add thermal mass and slow the response. For reference, the thermal diffusivity of typical metals are in the range of  $10^{-6}$  to  $10^{-4}$  m<sup>2</sup>/s [3]. Consequently, one might expect a 100 micron diameter wire to require on the order of  $10^{-4}$ – $10^{-2}$  seconds to equilibrate to the surrounding temperature, depending upon the metals used in its construction. Such preliminary estimates of thermocouple behavior have recently been shown to be somewhat misleading, however [4]. It has been demonstrated that commercially available 75 micron thermocouples can respond to sudden temperature jumps with a signal rise time of 10  $\mu$ s or even less. The implication seems to be that the entire junction of the thermocouple need not to come to thermal equilibrium in order to generate an output voltage that tracks the surrounding

temperature to within ~100 K. The fall time of the signal is, however, somewhat slower, and is consistent with the thermal mass of the junction and any attached substrates or armor.

Cold wire probes on the other hand have not been found to exhibit this anomalous behavior, presumably due to the fact that the resistance of the wire is dependent upon the temperature throughout its cross section. They have however been shown to be capable of high response rates of (5 kHz or more is achievable) in fluid flows with velocities of several hundred m/s [5]. The downside is that they are very fragile and break easily. To our knowledge no one has yet successfully attempted to utilize them in an explosive environment.

### **5.3 EMERGING TECHNOLOGIES**

One very clever approach currently being developed at AFRL [6] is to use arrays of co-located thermocouples with each thermocouple in the array having a different diameter and hence different response time. The signals from each thermocouple are recorded during the explosion, and then the thermal history is recovered by assuming that each thermocouple witnessed the same time-dependent temperature input. Heat flow modeling is used to solve for the single  $T(t)$  input that produces all of the observed thermocouple traces. While the inherent response times of the thermocouples themselves are still insufficient to fully resolve the thermal history of the event, this technique minimizes this shortcoming to some extent at the expense of requiring sophisticated post-processing of the data in order to quantitatively analyze it. It should also be noted that since the analysis involves extrapolating the data to “zero response time” thermocouple behavior, the extrapolation can become unreliable if the thermal input varies on a timescale that is more than a factor of 3-4 faster than the fastest thermocouple in the array.

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## **6. SENSOR PARTICLES**

### **6.1 OVERVIEW**

Nano/microparticle sensors are distinct from previous techniques discussed in this report in the sense that they are intended to provide information on the temperature experienced by small particles

(e.g., Bt) as they move during the “Agent Defeat” tests, even in extreme conditions and within an opaque fireball. Several techniques have now been proposed and some are in an advanced stage of development, with tests being conducted at the Naval Surface Warfare Center, Indian Head Division (NSWC-IHD), by Dr. Jim Lightstone and Dr. Jillian Horn, and the University of Illinois by Dr. Nick Glumac. Several results are already published [1-8].

These nano/microparticle sensors rely essentially on three types of thermally-driven physical mechanisms: phase changes of crystalline materials, morphological changes in nanostructures, and thermally stimulated recombination of electron-hole pairs trapped in lattice defects in crystalline materials. In a broad sense, the techniques probe the transition of the system from an unstable or metastable state to a state of lower energy.

As opposed to traditional fluorescence thermometry, in which the fluorescence from the particles is probed *in situ* under optical excitation [9-12], in the techniques described here the physical modifications experienced by the particles are measured *ex-situ*, after the event. This is achieved by measuring, for example, spectroscopy properties of the particles (absorption, Raman), the photoluminescence spectra of specific dopants, or the thermoluminescence from the particles.

Sensor particle techniques provide very different information than optical and physical probe measurements due to their ability to flow with the fluid of the explosion. Because of their small sizes, they should also respond very fast to the rapid changes in the temperature profile.

## **6.2 TECHNIQUES**

### **6.2.1 Irreversible morphology evolution of nanostructures**

Morphological changes in nanostructures have been explored as a method of temperature sensing by the group led by Dr. Jie Lian (Rensselaer Polytechnic Institute). The approach consists in using ultrathin gold island films (~1-5 nm) which are unstable and can disintegrate when heated through a process termed solid-state dewetting, reorganizing by evaporation-condensation and surface diffusion into structures of lower surface-to-volume ratio [7]. These morphological changes can be characterized using scanning electron microscopy (SEM) or atomic force microscopy (AFM), but the analysis is too slow. Instead, Dr. Lian’s group proposes to use ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy, taking advantage of the fact that surface plasmon (SP) absorption bands are significantly affected by the particle size, size distribution, shape and spacing of the nanostructures, among other factors [7]. The measurements consist in optical absorption measurements using commercial equipment (e.g., Cary UV/vis/NIR spectrophotometer).

Initial results on gold films on quartz substrate required temperature exposures that were too long for practical application, on the order of hundreds of seconds [7]. More recently, the group has proposed the observation of morphological changes in SiO<sub>2</sub>-Au core-shell structures (gold shell on silica core) with sizes of ~500-1000 nm for temperature sensing, also by UV-vis-NIR spectroscopy. Temperature-dependent changes in the surface-plasmon absorption band wavelength were observed for exposure times between 0.1 s and 1 s, with the highest sensitivity in the 400 – 800 °C range. These tests have been performed using Pyroprobe (CDS Analytical, Inc.).

Methods to extract the time-temperature profile are still under development and will require the use of at least two particles with different sizes or thermal responses. Experiments are planned using laser



heating and shock heating to test the nanoparticles at faster response times. Other innovative concepts include the use of graphene-wrapped nano-composites which, in addition to being highly thermally conductive, can crack distinctively under thermal loads, providing an additional method to measure temperature.

### 6.2.2 Increase in nanoparticle size

Dr. Liping Huang's group (Rensselaer Polytechnic Institute) proposed to use the size of  $\text{TiO}_2$  nanoparticles as the thermometric property. Upon heating, the size of the particles grow from  $\sim 5$  nm to  $>30$  nm. Due to size effects created by phonon confinement, the size of the nanoparticles can be determined using Raman spectroscopy by observing either the shift in the Raman frequency or changes in peak width [8]. For applications, the particles have to be placed in a substrate to serve as their carrier and protector, without interfering with the Raman spectrum.

$\text{TiO}_2$  nanoparticles were produced with two different structures, anatase and rutile, whose Raman spectra exhibit different changes upon heating [8]. Since each particle follows a pre-determined grain growth equation, the system of equations can be solved using data from two particles to determine both time and temperature, assuming a constant temperature profile. More particles would be necessary to reconstruct a more complex time-temperature profile.

Dr. Huang's group tested the technique using Pyroprobes with results in good agreement between the setting and calculated temperature for temperatures in the  $400 - 700$  °C range and times from  $5 - 60$  s. For shorter periods, the changes in the Raman spectra are too small. The technique remains to be tested inside a fireball.

Questions have been raised on the pressure effects on the diffusion equation and on the stability of the particles in high temperature, low oxygen environments. This also needs to be investigated, but there is the expectation that these phonon confinement properties can be observed in other oxides that may be stable under these conditions.

### 6.2.3 Irreversible phase changes in luminescent nanoparticles

Changes in the crystalline structure of oxides such as  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$  have been explored for temperature sensing by the group of Dr. Hergen Eilers (Washington State University). Heating of amorphous Eu-doped  $\text{Y}_2(\text{CO}_3)_3$  synthesized by co-precipitation converts the material to Eu-doped  $\text{Y}_2\text{O}_3$  [1, 3]. In a similar way, heating causes the crystallization of  $\text{Eu}_{0.01}\text{Zr}_{0.99}(\text{OH})_4$ , also synthesized by co-precipitation, into monoclinic and tetragonal phases of Eu-doped  $\text{ZrO}_2$  [2]. The particles consist of an agglomerate of particles with tens of nanometers in diameter [3].

In both cases, the crystal structure can be probed by monitoring the fluorescence excitation or emission spectra. The amorphous phases of such materials are characterized by broad excitation and emission bands, whereas crystalline phases are characterized by sharp  $\text{Eu}^{3+}$  lines. Furthermore, the emission lines of  $\text{Eu}^{3+}$  are very sensitive to the defect's crystal environment, which affect the  ${}^7\text{F}_1$  and  ${}^7\text{F}_2$  energy levels splitting and the probability transitions associated with the different  ${}^5\text{D}_0$ - ${}^7\text{F}_j$  transitions [13]. Therefore, changes in the crystal structure and defect environment can be detected by monitoring the relative intensity of distinct  $\text{Eu}^{3+}$  emission/excitation lines, their fluorescence lifetimes, peak positions, or line widths. This is achieved by exciting the samples with appropriate wavelength using light from a

laser-pumped optical parametric oscillator (OPO), while detecting the fluorescence spectrum using a monochromator or spectrometer with a PMT or CCD array.

In the case of  $\text{Y}_2\text{O}_3\text{:Eu}$ , the best temperature indicator seems to be the excitation peak positions and peak widths, whereas for  $\text{ZrO}_2\text{:Eu}$ , it is the ratio between the emission lines at 591.4 nm and 592 nm or the peak shift [2]. In the case of  $\text{Y}_2\text{O}_3\text{:Eu}$ , temperature measurements can be performed from ~300 - 700 °C range. For,  $\text{ZrO}_2$  the temperature range is from ~600 – 900 °C. Tests have been performed using the Pyroprobe (CDS Analytical, Inc.) at nominal ramp rates of 20,000 °C/s, heating times from 1 – 10 s, and temperatures ranging from 100 °C to 1100 °C.

Samples have been tested at the NSWC-IHD with preliminary results showing temperatures compatible with thermocouple measurements (i.e., slightly higher than thermocouples, which are known to underestimate the temperatures). At present the analysis relies on calibration of the material using the Pyroprobes. Results on  $\text{Y}_2\text{O}_3\text{:C}$  seem to indicate that the effect of temperature is stronger than time [1]. Ideas to be explored include the use of core/shell nanostructures to achieve a broader temperature range than  $\text{Y}_2\text{O}_3\text{:Eu}$  or  $\text{ZrO}_2\text{:Eu}$  particles.

#### **6.2.4 Thermally stimulated recombination of trapped electron-hole pairs**

The groups of Dr. Joseph Talghader (University of Minnesota) and Dr. Eduardo Yukihara (Oklahoma State University) are jointly developing a technique that monitors the concentration of trapped charges in the crystals as the thermometric property. When a crystal is exposed to ionizing radiation, a population of free electrons and holes is created and become trapped at intrinsic or extrinsic (impurity) defects in the crystal lattice. Upon heating, the probability that these trapped charges will escape from the traps increases, leading to recombination of the electron-hole pairs and luminescence, which is called thermoluminescence (TL) [14]. Exposure of the materials to a temperature profile leads to the selective depopulation of the traps that are least thermally stable, leaving other stable traps unchanged or with little change.

The surviving concentration of trapped electron-hole pairs can be monitored in laboratory using TL, by heating the material in a controlled way (typically linearly) while monitoring the light intensity using a photomultiplier tube. The resultant curve of light *versus* temperature contains several peaks associated with the concentration of trapped charges at different defects, which are affected differently by the temperature and time of exposure. The intensity of the different peaks, both absolute and relative, indicates which traps were affected during exposure to the temperature profile, therefore allowing the determination of the time and temperature of exposure (under certain assumptions) [6]. These measurements can be performed using microheaters developed at University of Minnesota or commercial TL readers used in dosimetry or luminescence dating (e.g. Risø TL/OSL reader, Risø National Laboratory, Denmark). A single particle typically has multiple trapping centers, which means that the use of multiple particles is not strictly necessary to obtain time and temperature. Moreover, different particles engineered with different luminescence centers can be used in a single detonation test; the TL can be measured separately in laboratory using appropriate optical filters.

Tests have been performed at the NSWC-IHD using a commercial TL material ( $\text{LiF:Mg,Ti}$ ) and three new materials developed by Oklahoma State University ( $\text{Li}_2\text{B}_4\text{O}_7\text{:Ag,Cu}$ ,  $\text{MgB}_4\text{O}_7\text{:Dy,Li}$ , and  $\text{CaSO}_4\text{:Ce,Tb}$ ), and new tests are currently taking place at University of Illinois. In addition, laboratory

tests are being conducted using flash paper, microheaters, and a temperature chamber. For tests that resulted in measurable changes in the TL, the temperatures were in agreement with thermocouple (or oven temperature). The TL materials have peaks at 200 – 400 °C if recorded at 1 °C/s, which means that the materials should be sensitive to higher temperatures in case of fast heating profiles (up to ~500 °C or more). Commercial readers can record the TL up to 700 °C, so extending the temperature range is a matter of developing materials with the appropriate trapping centers [15].

As opposed to other techniques described in this Section, TL particles require a pre-exposure treatment: the particles must be irradiated to create the population of trapped electrons and holes. On the other hand, the process is reversible: the signal can be regenerated after readout by re-irradiation, meaning that the amount of TL material present in the sample collected can be evaluated. This is helpful to determine if a zero TL signal is because the sample was heated to a very high temperature (in which case there will be regenerated TL) or because no material was recovered (in which case no regenerated TL is observed).

As observed for phase changes (Section 6.2.3), the effect of temperature seems to be stronger than the effect of time and the measurements are weighted towards the highest temperatures. Algorithms to recover the time-temperature profile are under development and have already been applied to tests at NSWC-IHD. The main challenge is to model the TL materials with sufficient detail to predict the effect of any heating profile on the TL curves and, if necessary, develop new TL materials with appropriate defects.

### **6.3 REMARKS**

One common challenge to all techniques described here is the problem of separating the effects of time and temperature. Most, if not all, processes described are governed by the Boltzmann factor  $e^{-E/kT}$ , which expresses the effect of temperature, and a pre-exponential factor that determines the time dependence. The total effect of a temperature profile on the thermometric quantity depends on the integral of this product over time, preventing the separation of time and temperature without further assumptions. Nevertheless, it has been noted by different investigators that the effect of temperature is stronger than the effect of time, which means that if the timescale of the process is known, the temperature can be obtained with a good accuracy, in spite of uncertainties in the duration.

One difference between the techniques is that most require different materials or particles to separately evaluate the effects of time and temperature. This is complicated by the fact that, unless they are combined in a nanocomposite or in a core-shell nanostructure, the particles may experience different temperature profiles. TL particles contain multiple trapping centers within the same particle and, in principle, do not require the use of multiple particles.

In all cases, the measurements are carried out using either standard or commercial equipment. The main challenges are related to development of materials with sensitivity in the appropriate temperature range, characterization of the materials and of the kinetics of the thermally driven processes, and development of algorithms to extract the temperature profiles from the data.

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